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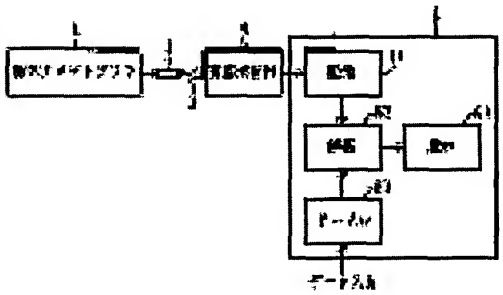
(54) MASS SPECTROMETRY METHOD AND DEVICE

(57)Abstract:
PROBLEM TO BE SOLVED: To speedily and accurately estimate a pseudo molecular ion and furthermore the molecular weight of a sample by preventing an error from being generated.
SOLUTION: An analysis part 62 searches a peak that exceeds a threshold level on a mass spectrum, adds a mass to the mass difference of an addition ion table being stored in a table 63, and creates a pseudo mass spectrum. The analysis part 62 compares the created pseudo mass spectrum with the mass of an obtained spectrum. Then, when both masses are the same, the analysis part 62 adds 1 to an index and calculates a final index. Then, another mass peak that exceeds the threshold level is searched and is processed in the same way. An obtained index value is compared and the possibility of m/z (the ratio of the mass of ion to the charge) and added ions is indicated at a display part 64. Then, an appearance frequency for each kind of detected ions is counted and is stored in, for example, a storage means. If a specific number of measurements is executed, weighting is made in the order of ion seeds with a higher frequency and the additional ion table of the table 63 is updated.



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[Claim(s)]

[Claim 1] In the mass analysis method which carries out analysis processing of the mass spectrum acquired under atmospheric pressure or the pressure of the near by introducing the ion which generated ion and was generated and carrying out mass analysis The account of a top the mass difference between the mass as which it was chosen of in the acquired mass spectrum, and other mass It asks for which is in agreement with two or more mass differences between the pseudo-molecular ion beforehand memorized by the adduct-ion storage means and two or more adduct-ion kinds as an index. The mass analysis method characterized by presuming the ion from which the number whose above-mentioned mass difference corresponds serves as size most to be a pseudo-molecular ion based on this index for which it asked.

[Claim 2] In the mass analysis method according to claim 1, the adduct ion of the presumed pseudo-molecular ion Memorize for every one mass analysis and it asks for the number of the frequencies of occurrence of the memorized adduct ion in the mass analysis of the predetermined number of times. The mass analysis method characterized by performing weighting to two or more above-mentioned adduct-ion kinds, making the above-mentioned adduct-ion storage means memorize this weighting according to this number of the frequencies of occurrence for which it asked, adding this memorized weighting to the above-mentioned index, and presuming a pseudo-molecular ion.

[Claim 3] Setting to the mass analysis method according to claim 1, the acquired mass spectrum is the mass analysis method characterized by being the mass spectrum which deducted the background spectrum which is a mass spectrum of the portion into which the component which should be analyzed has not appeared from the mass spectrum which carried out mass analysis the account of a top.

[Claim 4] The mass analysis method characterized by for two or more mass differences between a pseudo-molecular ion and two or more adduct-ion kinds being memorized by the kind of solvent used for mass analysis by the above-mentioned adduct-ion storage means, the kind of ionization, and two or more storage tables divided for every polarity of a spectrum, and a suitable storage table being chosen as them by the analysis conditions of mass analysis in the mass analysis method according to claim 1, 2, or 3.

[Claim 5] Setting to the mass analysis method according to claim 1, 2, 3, or 4, the acquired mass

spectrum is the mass analysis method characterized by being the mass spectrum which amended 13C to the mass spectrum which carried out mass analysis the account of a top.

[Claim 6] It is the mass analysis method characterized by displaying the above-mentioned mass spectrum by the bar graph, discriminating the bar of a bar graph in which the mass peak presumed as a pseudo-molecular ion and an adduct ion of this is shown from the size of the bar of a bar graph which the size or a color display shows other mass peaks which are not presumed, or a color display, and displaying it in the mass analysis method according to claim 1, 2, 3, 4, or 5.

[Claim 7] The mass spectroscope which has a means to generate ion under the atmospheric pressure characterized by providing the following, or the pressure of the near, the mass spectrometer which introduces and carries out mass analysis of the generated ion, and the data-processing means which carries out analysis processing of the mass spectrum outputted from this mass spectrometer. The above-mentioned data-processing means is an adduct-ion storage means to memorize two or more mass differences between a pseudo-molecular ion and two or more adduct-ion kinds. The analysis section which presumes the ion from which the number whose above-mentioned mass difference asks for whether the mass difference of which between the mass as which it was chosen of in the mass spectrum acquired the account of a top, and other mass corresponds with two or more mass differences memorized by the above-mentioned adduct-ion storage means as an index, and corresponds based on this index for which it asked serves as size most to be a pseudo-molecular ion.

[Claim 8] In a mass spectroscope according to claim 7 the above-mentioned analysis section The adduct ion of the presumed pseudo-molecular ion is memorized for every one mass analysis. It asks for the number of the frequencies of occurrence of the memorized adduct ion in the mass analysis of the predetermined number of times. The mass spectroscope characterized by performing weighting to two or more above-mentioned adduct-ion kinds, making the above-mentioned adduct-ion storage means memorize this weighting according to this number of the frequencies of occurrence for which it asked, adding this memorized weighting to the above-mentioned index, and presuming a pseudo-molecular ion.

[Claim 9] It is the mass spectroscope characterized by deducting the background spectrum which is a mass spectrum of the portion into which the component which should be analyzed has not appeared, and the above-mentioned analysis section presuming a pseudo-molecular ion about this deducted mass spectrum from the mass spectrum to which the above-mentioned data-processing means was outputted from the above-mentioned mass spectrometer in the mass spectroscope according to claim 7.

[Claim 10] It is the mass spectroscope which two or more mass differences between a pseudo-molecular ion and two or more adduct-ion kinds are memorized by the kind of solvent used for mass analysis by the above-mentioned adduct-ion storage means in a mass spectroscope according to claim 7, 8, or 9, the kind of ionization, and two or more storage tables divided for

every polarity of a spectrum, and is characterized by the above-mentioned analysis section choosing a suitable storage table according to the analysis conditions of mass analysis.

[Claim 11] It is the mass spectroscope characterized by the above-mentioned analysis section presuming a pseudo-molecular ion about the mass spectrum which amended 13C to the mass spectrum to which the above-mentioned data-processing means was outputted from the above-mentioned mass spectrometer in the mass spectroscope according to claim 7, 8, 9, or 10, and performed this amendment.

[Claim 12] In a mass spectroscope according to claim 7, 8, 9, 10, or 11 the above-mentioned data-processing means It has the data display section further. the above-mentioned data display section The bar of a bar graph in which the mass peak which displayed the above-mentioned mass spectrum by the bar graph, and was presumed as a pseudo-molecular ion and an adduct ion of this is shown The mass spectroscope to which the size or a color display is characterized by what it discriminates from the size of the bar of a bar graph or color display which shows other mass peaks which are not presumed, and is displayed.

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the optimal mass spectrum analytical method and optimal equipment in quest of a molecular ion, as a result molecular weight from the mass spectrum acquired especially by atmospheric pressure ionization with respect to the analytical method of the mass spectrum acquired with the mass spectrometer.

[0002]

[Description of the Prior Art] A mass spectrometry is a very high sensitivity measuring method [not only], but an outstanding analysis method which gives the molecular weight and the structure information on a sample. Furthermore, separation meanses, such as a gas chromatograph and a liquid chromatograph, are prepared in the preceding paragraph of a mass spectroscope, the equipment which carries out direct separation analysis of the mixture is developed, and it came to be used widely recently.

[0003] Generally, it is first ionized by the ion source, mass distribution is carried out in the mass analysis section, and the sample molecule introduced into the mass spectrometer is detected by the detector, and can acquire a mass spectrum.

[0004] In this case, the mass spectrum acquired is expressed as a bar graph as shown in drawing 3 . As for a horizontal axis (X-axis), this drawing 3 shows the mass pair charge ratio (m/z) of ion, and the vertical axis (Y-axis) shows the relative intensity of each ion by which the normalize was carried out by making the strongest peak into 100%.

[0005] A mass spectrum consists of fragmentation (fragment) ion (two or more 200 or less m/z ion

when it is the example of drawing 3), adduct ions (larger ion than m/z200), etc. in which the molecular ion (m/z200 when it is the example of drawing 3) by which the molecule itself was ionized, and the molecular ion broke.

[0006] Moreover, as shown in drawing 9 recently, the liquid chromatograph (LC) 1 combines with a mass spectrometer 4 as a separation means, and the liquid chromatograph direct connection mass-spectrometer system (LC/MS) of form that ionization is performed under atmospheric pressure began to spread. What has spread most as atmospheric pressure ionization in this case is with the electrospray method (Electro-Spray, ESI) and an atmospheric pressure chemical ionization method (Atmospheric Pressure Ionization, APCI).

[0007] In ESI, the drop by which it was electrified is generated by leading to the nozzle (ESI probe) 2 with which the eluate from LC1 was impressed to the high voltage, and spraying the drawn eluate into high electric field from this nozzle 2. This drop is made to collide with an air molecule etc., misty detailed-izing and misty dryness are performed, and ion 3 is generated.

[0008] On the other hand, an atmospheric pressure chemical ionization method (APCI) ionizes a sample molecule by ion molecular reaction. The needle with which the high voltage was impressed to the lower stream of a river of the sprayed drop is arranged. The solvent molecule which exists in large quantities is first ionized by the corona discharge generated from this needle. Solvent ion collides with a surrounding molecule further, and, finally ionizes a sample molecule. It mass-distributes, ion is detected by the mass spectrometer 4, and a mass spectrum is acquired by the data processor 5.

[0009] the pseudo-molecular ion which a proton and alkali-metal ion (Na+ ion etc.) added to the molecule while both [these] ionization of a fragment ion could not be completed easily, since it was soft (the energy in the case of ionization is small) ionization -- intensity -- it is generated highly Therefore, an unstable compound etc. is stably ionizable.

[0010] After ionization exists [the ion which generated atmospheric pressure ionization for the ionization under atmospheric pressure] under atmospheric pressure. Therefore, a surrounding neutral molecule (in the cases of many molecule of a solvent) and a collision are repeated. Moreover, the ion generated under atmospheric pressure is introduced into the vacuous room, and mass analysis is carried out. Ion is quickly cooled by rapid expansion (adiabatic expansion) in the case of the introduction to this vacuum chamber.

[0011] If the solvent molecule cooled like the cooled ion collides with ion, the adduct ion which is no longer separated from ion in a solvent molecule, and many polar molecules (solvent molecule) added will be made. Since the ion which should become one mass peak (molecular ion) originally distributes to two or more adduct ions, this adduct ion will lower the intensity of a molecular ion.

[0012] Consequently, molecular ion SN ratio ****** will lower the detection sensitivity of equipment remarkably seemingly. Moreover, since a mass spectrum becomes complicated, the appearance of this adduct ion serves as analytic hindrance. Therefore, commercial LC/MS

equipment has meanses (heating, collision activation maceration of ion, etc.) to make an adduct ion dissociate. Consequently, in the mass spectrum generally acquired by commercial LC/MS equipment, the intensity of an adduct ion is very small.

[0013] However, if a mass spectrum is seen in detail, in many cases, these adduct ions are observable in many cases.

[0014] Generally the addition energy at the time of a polar molecule adding to ion is 1eV or less, and is very small compared with the binding energy of the chemical bonds (C-C, C-H combination, etc.) which constitute ion.

[0015] Therefore, when superfluous energy (acceleration of heat or ion, collision, etc.) joins a molecular ion and a fragment ion arises, an addition molecule dissociates first. It becomes after that that covalent bond goes out and a fragment ion generates. Therefore, the adduct ion which the polar molecule added to the fragment ion does not usually exist.

[0016]

[Problem(s) to be Solved by the Invention] For the ionization with soft atmospheric pressure ionization, there are few fragment ions, and as shown in drawing 10 , they give the simple mass spectrum as which the pseudo-molecular ion (protonation ion) was emphasized. However, this simplicity will lack the conclusive factor of molecular weight determination conversely.

[0017] When it is the electronic ionizing method (Electron Ionization, EI) many fragment ions appear, the mass difference between the ion presumed to be a molecular ion and two or more fragment ions is searched for, and presumption which is made to contrast the generation process (for it to be flag MENTESHONTO **** about this) of fragmentation, and does not have conflict by the molecular ion is carried out. Reasoning will be more right if many fragment ions can be explained without conflict.

[0018] However, generally, the mass spectrum of LC/MS has many bird clappers very simply, as shown in drawing 10 . In this case, it is because it cannot judge immediately whether the ion which has appeared is a pseudo-molecular ion and a fragment ion in which it and it broke, or it is the ion which the solvent molecule added. Therefore, in order to presume a pseudo-molecular ion, you have to presume molecular weight through the process of the following complicated trial and error.

[0019] That is, in the high mass field in the mass spectrum acquired in the mass spectrum, the strongest peak is first assumed to be a pseudo-molecular ion. Next, a mass difference with the ion of this this mass peak and mass peak circumference is searched for. And it investigates one by one whether these mass differences are in agreement with the molecular weight of a solvent molecule or ammonium ion. If in agreement, the possibility of an adduct ion will judge it as a dovetail once.

[0020] Next, the mass peak of another mass is assumed to be a pseudo-molecular ion, and a pseudo-molecular ion is presumed through the same process. What has the fewest conflict in a

repetition of these trial and error is presumed to be a pseudo-molecular ion.

[0021] However, presumed analysis mentioned above is performed by human beings, such as an analysis person, and the process of this presumed analysis has only repeated trial and error. Therefore, prejudgment tends to enter into presumption and assumption and, naturally it is easy to generate an oversight and misapprehension. After all, a fault and the possibility of overlooking become very high. Moreover, time and a result which consumes an effort in large quantities are brought.

[0022] The possibility of appearances, such as an adduct ion, is greatly influenced by the physicochemical quality of a compound, LC analysis conditions (the kind of eluate, PH, the rate of flow, temperature, etc.), the measurement conditions of LC/MS equipment (the voltage of ESI, APCI, or an interface, temperature, pressure, etc.), etc. It is necessary to perform analysis by considering these prerequisites.

[0023] Therefore, sophistication and a long experience are required of the analysis of the mass spectrum of a strange component. Generally, since it differs from an operating personnel and an analysis person in many cases, no analysis conditions will be told by the analysis person from an operating personnel, but an error will enter into analysis.

[0024] Furthermore, when two or more components overlap and it is eluted from LC, or when a measurement sample is mixture, a mass spectrum turns into a spectrum of mixture. And a mass spectrum becomes complicated in this case, and the analysis of this mass spectrum becomes difficult [a experienced person].

[0025] Moreover, in measurement of LC/MS, acquiring 1000 or more mass spectrums is usually performed to a day. The analysis of the mass spectrum acquired in large quantities needs many time and efforts, and must stop therefore, having to spare time for analysis beyond measurement. therefore -- naturally -- the error of analysis -- generating -- ****** -- ** This serves as big hindrance of the improvement in efficiency of LC/MS qualitative analysis.

[0026] The purpose of this invention is [0027] which is preventing a fault entering quickly and realizing the mass analysis method and equipment which can presume the molecular weight of a pseudo-molecular ion, as a result a sample with high precision.

[Means for Solving the Problem]

(1) In order to attain the above-mentioned purpose, this invention is constituted as follows. Namely, it sets to the mass analysis method which carries out analysis processing of the mass spectrum acquired under atmospheric pressure or the pressure of the near by introducing the ion which generated ion and was generated and carrying out mass analysis. The account of a top the mass difference between the mass as which it was chosen of in the acquired mass spectrum, and other mass It asks for which is in agreement with two or more mass differences between the pseudo-molecular ion beforehand memorized by the adduct-ion storage means and two or more adduct-ion kinds as an index, and it is constituted so that the ion from which the number whose

above-mentioned mass difference corresponds serves as size most may be presumed to be a pseudo-molecular ion based on this index for which it asked.

[0028] Quickly [since it is constituted possible], presuming a molecular ion automatically can prevent a fault entering, and it can realize a pseudo-molecular ion, as a result the mass analysis method that the molecular weight of a sample can be presumed with high precision.

[0029] (2) In the above (1), preferably the adduct ion of the presumed pseudo-molecular ion Memorize for every one mass analysis and it asks for the number of the frequencies of occurrence of the memorized adduct ion in the mass analysis of the predetermined number of times. Perform weighting to two or more above-mentioned adduct-ion kinds, and the above-mentioned adduct-ion storage means is made to memorize this weighting according to this number of the frequencies of occurrence for which it asked, and this memorized weighting is added to the above-mentioned index, and presumes a pseudo-molecular ion.

[0030] About an ion kind with the high frequency of occurrence, weighting can be carried out and the mass analysis precision of the analysis object analyzed by each mass spectroscope since it constitutes so that it may carry out which an adduct-ion storage means is made to memorize can be improved. [many]

[0031] (3) Moreover, in the above (1), the acquired mass spectrum is a mass spectrum deducted from the mass spectrum in which the background spectrum which is a mass spectrum of the portion into which the component which should be analyzed has not appeared carried out mass analysis the account of a top preferably.

[0032] (4) Moreover, preferably, in the above (1), (2), or (3), two or more mass differences between a pseudo-molecular ion and two or more adduct-ion kinds are memorized by the above-mentioned adduct-ion storage means, and a suitable storage table is chosen as the kind of solvent used for mass analysis, the kind of ionization, and two or more storage tables divided for every polarity of a spectrum according to the analysis conditions of mass analysis.

[0033] Since a suitable storage table is chosen by the analysis conditions of mass analysis, according to them, the optimal presumption of a pseudo-molecule according to analysis conditions is attained.

[0034] (5) Moreover, in the above (1), (2), (3), or (4), the acquired mass spectrum is a mass spectrum which amended 13C to the mass spectrum which carried out mass analysis the account of a top preferably.

[0035] It sets preferably to the above (1), (2), (3), (4), or (5). (6) Moreover, the above-mentioned mass spectrum It is displayed by the bar graph, and the size or a color display is discriminated from the size of the bar of a bar graph or color display which shows other mass peaks which are not presumed, and the bar of a bar graph in which the mass peak presumed as a pseudo-molecular ion and an adduct ion of this is shown is displayed.

[0036] Since the bar of a bar graph in which the mass peak presumed to be a pseudo-molecular

ion is shown is shown by the bar thicker than other mass peaks, a pseudo-molecular ion can be shown clearly.

[0037] (7) Moreover, a means to generate ion under atmospheric pressure or the pressure of the near, In the mass spectroscope which has the mass spectrometer which introduces and carries out mass analysis of the generated ion, and the data-processing means which carries out analysis processing of the mass spectrum outputted from this mass spectrometer An adduct-ion storage means by which the above-mentioned data-processing means memorizes two or more mass differences between a pseudo-molecular ion and two or more adduct-ion kinds, The account of a top the mass difference between the mass as which it was chosen of in the acquired mass spectrum, and other mass It asks for which is in agreement with two or more mass differences memorized by the above-mentioned adduct-ion storage means as an index, and has the analysis section which presumes the ion from which the number whose above-mentioned mass difference corresponds serves as size most to be a pseudo-molecular ion based on this index for which it asked.

[0038] Quickly [since it is constituted possible], presuming a molecular ion automatically can prevent a fault entering, and it can realize a pseudo-molecular ion, as a result the mass spectroscope which can presume the molecular weight of a sample with high precision.

[0039] It sets above (7) preferably. (8) The above-mentioned analysis section The adduct ion of the presumed pseudo-molecular ion is memorized for every one mass analysis. It asks for the number of the frequencies of occurrence of the memorized adduct ion in the mass analysis of the predetermined number of times. Perform weighting to two or more above-mentioned adduct-ion kinds, the above-mentioned adduct-ion storage means is made to memorize this weighting according to this number of the frequencies of occurrence for which it asked, this memorized weighting is added to the above-mentioned index, and a pseudo-molecular ion is presumed.

[0040] About an ion kind with the high frequency of occurrence, weighting can be carried out and the mass analysis precision of the analysis object analyzed by each mass spectroscope since it constitutes so that it may carry out which an adduct-ion storage means is made to memorize can be improved. [many]

[0041] (9) Moreover, preferably, in the above (7), the above-mentioned data-processing means deducts the background spectrum which is a mass spectrum of the portion into which the component which should be analyzed has not appeared from the mass spectrum outputted from the above-mentioned mass spectrometer, and the above-mentioned analysis section presumes a pseudo-molecular ion about this deducted mass spectrum.

[0042] (10) Moreover, preferably, in the above (7), (8), or (9), two or more mass differences between a pseudo-molecular ion and two or more adduct-ion kinds are memorized by the kind of solvent used for mass analysis, the kind of ionization, and two or more storage tables divided for every polarity of a spectrum, and the above-mentioned analysis section chooses a suitable

storage table as the above-mentioned adduct-ion storage means according to the analysis conditions of mass analysis.

[0043] Since a suitable storage table is chosen by the analysis conditions of mass analysis, according to them, the optimal presumption of a pseudo-molecule according to analysis conditions is attained.

[0044] (11) Moreover, preferably, in the above (7), (8), (9), or (10), the above-mentioned data-processing means amends 13C to the mass spectrum outputted from the above-mentioned mass spectrometer, and the above-mentioned analysis section presumes a pseudo-molecular ion about the mass spectrum which performed this amendment.

[0045] It sets preferably to a mass spectroscope the above (7), (8), (9), (10), or given in (11). (12) Moreover, the above-mentioned data-processing means It has the data display section further. the above-mentioned data display section The above-mentioned mass spectrum is displayed by the bar graph, and it discriminates from the size of the bar of a bar graph or color display which shows other mass peaks the size or the color displays is not presumed to be in the bar of a bar graph in which the mass peak presumed as a pseudo-molecular ion and an adduct ion of this is shown, and displays.

[0046] Since the bar of a bar graph in which the mass peak presumed to be a pseudo-molecular ion is shown is shown by the bar thicker than other mass peaks, a pseudo-molecular ion can be shown clearly.

[0047]

[Embodiments of the Invention] Drawing 1 is the outline block diagram of the mass spectroscope which realizes the mass analysis method which is the 1st operation gestalt of this invention, it is an example at the time of applying to a liquid chromatograph (LC), and the same sign is given to the portion equivalent to the example shown in drawing 9 .

[0048] In drawing 1 , the mass spectrum of the mass analyzed by the mass spectrometer 4 is inputted into the mass-spectrum storage section 61 of a data processor 6, and is memorized. And the mass spectrum memorized by the mass-spectrum storage section 61 presumes a pseudo-molecular ion with reference to the adduct-ion table (adduct-ion storage means) on which the analysis section 62 was stored in the table 63 and which is mentioned later. The result analyzed by the presumed section 62 is displayed by the bar graph etc. by the display 64.

[0049] The adduct-ion table shown in Table 1 shows the adduct ion which it is [in the case of atmospheric pressure chemical ionization] good, and appears. In addition, this adduct-ion table and other adduct-ion tables mentioned later are obtained by the experiment by the artificers of this application. Moreover, since the dehydration peak at which the moisture child was desorbed from the protonated ion also serves as a conclusive factor of presumption of a pseudo-molecular ion in the table of the following adduct ions, it has added to the table.

[0050]

[Table 1]

質量差	イオン種	
－１８	脱水ピーク	フラグメントイオン
０	プロトン付加イオン	（Ｍ＋１）擬分子イオン
＋１７	アンモニウムイオン付加イオン	（Ｍ＋ＮＨ４）
＋３２	メタノール付加イオン	
＋４１	アセトニトリル付加イオン	
＋４９	アンモニア＋メタノール付加	
＋５８	アンモニア＋アセトニトリル付加	
＋６０	酢酸付加イオン	
＋７７	酢酸アンモン付加	

[0051] In this table 1, ammonia ion adduct-ion (M+NH4) + can be called one of the pseudo-molecular ions like protonation ion (M+H) +. A still more neutral solvent molecule etc. adds other ion to these pseudo-molecular ion. Generally the ion to which alkali-metal ion (Na and K ion) added APCI unlike ESI does not appear.

[0052] The adduct-ion table shown in Table 2 shows the pseudo-molecular ion and adduct ion which appear in an ESI spectrum.

[0053]

[Table 2]

質量差	イオン種
－１８	脱水ピーク
０	プロトン付加
＋１７	アンモニウムイオン付加イオン
＋２２	＋Ｎａ
＋３２	メタノール付加
＋３９	＋Ｋ
＋４１	アセトニトリル付加
＋４９	アンモニア＋メタノール
＋５４	＋Ｎａ＋メタノール
＋５８	アンモニア＋メタノール

質量差	イオン種
＋６０	酢酸付加
＋６３	＋Ｎａ＋アセトニトリル
＋７０	＋Ｋ＋メタノール
＋７７	酢酸アンモン付加
＋７９	＋Ｋ＋アセトニトリル

[0054] In Table 2, + (M+Na), (M+K)+ ion, etc. which alkali-metal ion besides a protonated ion added are observed well. The ion which the solvent molecule added to these ion as well as atmospheric pressure chemical ionization (APCI) appears well.

[0055] The adduct-ion table mentioned above can be inputted into a table 63 by the external input means.

[0056] Drawing 2 is a flow chart which shows operation by the whole analysis of the mass spectrum by the data processor 6. In Step 100 of drawing 2 , the analysis section 62 reads a mass spectrum from the mass-spectrum storage section 61.

[0057] Next, in Step 101, the analysis section 62 performs background processing and a normalize. Solvent ion and the ion of an impurity usually mix in the acquired mass spectrum. The background becomes remarkable when there are few amounts of the sample especially introduced into a mass spectrometer. This background In order to make next analysis start an error, a total is performed from the mass spectrum which is equivalent to a component by making into a background spectrum the mass spectrum of the portion into which the component

has not appeared.

[0058] And it asks for the relative intensity of other mass peaks in normalize processing, using the ion of the degree of strongest as 100. Comparison becomes possible [without this being dependent on the amount of the sample introduced into a mass spectrometer] with others and a mass spectrum.

[0059] Moreover, the peak according [an actual mass spectrum] to a noise near the base line exists. Since these are blocked in future comparison, it is necessary to remove them. For this reason, a threshold level is prepared, it considers as the object of comparison of only the peak beyond this, and the influence of a noise is eliminated.

[0060] Next, an isotopic peak is removed in Step 102. In natural carbon, about 1% of 13C is contained. By removing from a mass spectrum, next processing can increase the mass peak originating in the isotope of this carbon in correctness. The intensity of an isotope will be ****** **** if ionic strength will be multiplied by the carbon number if the number of the carbon which constitutes ion is known, and it asks for 1/100 of those further. However, generally it cannot ask for the number of the carbon atoms which constitute ion beforehand.

[0061] Then, suppose that a near carbon atom is presumed by approximation of the following in Step 102. Thereby, processing of the following pseudo-molecular-ion presumption is advanced.

[0062] Since the ratio of 13C/12C of contribution of the natural 13C isotope originating in the ion of the mass m of ionic strength Im is 1%, the amount contributed of an isotope can be approximated by the following formula (1) to the ion of mass m+1.

Imx(m/14) x0.01 --- (1)

Therefore, ionic strength Im+1' of the ion of mass m+1 which removed the amount contributed of an isotope is called for by the following formula (2).

Im+1'=Im+1-Imx(m/14) x0.01 --- (2)

Here, it is referred to as Im+1'=0 if it is Im+1'<0.

[0063] Now, when intensity of the ion of 100 and mass 201 is set to 20, the amount contributed of the isotope to the mass 201 of the ion of mass 200 can ask for the intensity of the ion of mass 200 by the following formula (3).

100x(200/14) x0.01=14.2 --- (3)

It is considered among the mass peak intensity 20 of mass 201 that about 14 is the isotopic peak of the ion of mass 200. Consequently, it is considered that 20-14=6 [6], i.e., intensity, are the ionic strength of original of mass 201. It is simplified as this processing shows the mass spectrum shown in drawing 3 to drawing 4 .

[0064] And in Step 104, the display output of the molecular ion presumed at Step 103 is supplied and carried out to the displays 64, such as CRT and a printer.

[0065] Next, detailed processing of search of the pseudo-molecular ion in Step 103 mentioned above is explained according to the flow chart of drawing 5 . The analysis section 62 searches for

the peak which exceeded the above-mentioned threshold level on the mass spectrum in Step 200 of drawing 5 . And if it searches for the peak, it will progress to Step 201.

[0066] In Step 201, the analysis section 62 adds mass m/z to the mass difference of the table (Table 1, table 2 grade which were mentioned above) of the adduct ion memorized by the table 63, and creates a false mass spectrum. And in Step 202, if the analysis section 62 measures the mass of the created false mass spectrum (there is no ionic strength) and the acquired spectrum and its mass of both corresponds, it will compute the final index S by adding 1 to Index S.

[0067] Next, it searches for other mass peaks exceeding a threshold level in Step 203. And in Step 204, if there is a mass peak which should be compared, Steps 201-203 which progressed to Step 201 and were mentioned above will be performed. In Step 204, if the mass peak which should be compared does not exist in others, it progresses to Step 205.

[0068] In Step 205, the value of the obtained index S is compared, it rearranges from the maximum, and the possibility of m/z and an adduct ion is displayed on the displays 64, such as CRT and a printer.

[0069] Next, in Step 206, in the processing mentioned above, the appearing number of frequency is counted for every detected ion kind, and it memorizes for the storage means in the analysis section 62 etc. And in Step 207, if only the number of times of predetermined is performed, measurement will perform weighting in order of an ion kind with the high number of frequency counted at Step 206, and will rewrite the adduct-ion table memorized by the table 63. And processing is ended.

[0070] The value to which weighting of the ion kind which corresponded in Step 202 was carried out is added to Index S. In the usual ion kind, this value added serves as the 1.5th grade, when it is 1, then an ion kind with the high frequency of occurrence.

[0071] Thus, about an ion kind with the high frequency of occurrence, weighting is carried out automatically, and since it constitutes so that an adduct-ion table may be updated, the mass analysis precision of the analysis object analyzed can be improved by each mass spectroscope. [many]

[0072] As mentioned above, according to the mass analysis method and equipment which are the 1st operation gestalt of this invention, since it is constituted by the data processor so that a molecular ion may be presumed automatically, it can prevent a fault entering quickly and the mass analysis method and equipment which can presume the molecular weight of a pseudo-molecular ion, as a result a sample with high precision can be realized.

[0073] Furthermore, since according to the 1st operation gestalt of this invention it constitutes so that weighting may be carried out automatically and an adduct-ion table may be updated in an automatic hand about an ion kind with the high frequency of occurrence, the mass analysis precision of the analysis object analyzed can be improved by each mass spectroscope. [many]

[0074] Drawing 6 is the operation flow chart of the mass analysis method which is the 2nd

operation gestalt of this invention. About the composition of the mass spectroscope which realizes the mass analysis method of this 2nd operation gestalt, since it becomes being the same as that of the composition in the 1st operation gestalt mentioned above, illustration and its explanation are omitted. Moreover, this 2nd operation gestalt is the method of asking for an index from a mass difference unlike the 1st operation gestalt mentioned above.

[0075] In Step 300 of drawing 6 , the analysis section 62 reads a mass spectrum from the storage section 61. Here, the mass spectrum pass subtraction of the background shall be shown in drawing 3 .

[0076] And an isotope is processed to the mass spectrum of this drawing 3 , and the mass spectrum shown in drawing 4 is obtained. Next, it searches for the peak which exceeded predetermined SURESUSHURUDO level from the read mass spectrum in Step 301. In the example of drawing 4 , it considers as mass 200, 217, 232, and 249.

[0077] Next, in Step 302, a peak with the smallest mass is selected among the selected peaks. In this case, it is mass 200. And in Step 303, the mass difference of the peak of the selected mass 200 and the mass (217, 232, 249) of the peak as which others were chosen is computed. In this case, 17, 32, and 49 are computed.

[0078] Then, in Step 304, the adduct-ion table memorized by the computed mass difference and the table 63 is compared, and if in agreement, it will count up. That is, as for an adduct-ion table, in the case of a cation, ionization uses the above-mentioned table 1 by APCI.

[0079] And it investigates whether the three above-mentioned mass differences exist in Table 1, and if a mass difference exists in front Naka, 1 will be added to Index S. In this case, since three mass differences agree, an index is set to 3.

[0080] And in Step 305, Score S, i.e., the obtained index, is memorized and the following mass peak is selected. In this case, mass 217 is chosen. Next, in Step 306, it judges whether there is any peak to compare.

[0081] In this case, since 200, 232, and 249 exist, the peak in comparison with mass 217 returns to Step 303. At Step 303, the mass difference of mass 217 and other ion is searched for. In this case, -17, and 15 and 32 are obtained.

[0082] Then, these mass difference and Table 1 are compared like Step 304 mentioned above. In this case, Index S is set to 1 in order for there to be only one agreeing thing. Henceforth, similarly, Steps 305 and 306 are performed, a pseudo-molecular ion is assumed one after another, and a mass difference is searched for, and Index S is computed and it goes. The result is shown below.

[0083]

[Table 3]

仮定された擬分子イオン	質量差	指標
２００	１７、３２、４９	３
２１７	－１７、１５、３２	１
２３２	－３２、－１５、１７	１
２４９	－４９、－３２、－１７	０

[0084] 200 whose index S is 3 has the highest possibility as a pseudo-molecular ion from the above-mentioned result.

[0085] Next, in Step 307, a score (index S) is rearranged and it outputs by the display 64 in an order from the highest score. Since the following steps 308 and 309 are the same as Steps 206 and 207 shown in drawing 5 , explanation is omitted.

[0086] Although the example mentioned above is progress which presumes a molecular ion from the mass spectrum shown in drawing 4 next, it explains the progress which presumes a molecular ion from the mass spectrum shown in drawing 7 .

[0087] The mass spectrum shown in this drawing 7 is a mass spectrum of mixture. Therefore, many ion has appeared on one mass spectrum. And the mass peak chosen in this case is set to 182, 200, 212, 217, 230, 232, 247, and 262. The these-chosen peak is asked for Index S according to the same process as **** and ****. The result is shown below.

[0088]

[Table 4]

No.	仮定擬分子イオン	質量差	指標
1	182	18、30、35、48 50、65、80	0
2	200	−18、12、17、30 32、47、62	3
3	212	−30、−12、5、18 20、35、50	0
4	217	−35、−17、−5、13 15、30、45	0
5	230	−48、−30、−18 −13、2、17、32	3
6	232	−50、−32、−20 −15、−2、15、30	0
7	247	−65、−47、−35 −30、−17、−15、15	0
8	262	−80、−62、−50 −45、−32、−30、−15	0

[0089] From the above-mentioned result, the index value 3 with No.2 of assumption and No.5 is shown. [same] In this case, it can be presumed that two components with the pseudo-molecular ions 200 and 230 are being mixed.

[0090] Thus, if the technique mentioned above is used, it compares, and even when a sample is mixture, a pseudo-molecular ion can be presumed correctly.

[0091] the table of an adduct ion shown above -- in addition, the table of the APCI, the ESI anion negative, or the ion shown below is also looked like [a table 63], and is memorized

[0092]

[Table 5]

ＡＰＣＩ、ＥＳＩ負イオン付加イオンのテーブル

質量差	イオン種	
0	プロトン脱離イオン	Ｍ－１
＋３２	メタノール付加	
＋３５	塩素付加	
＋６０	酢酸付加	$M+CH_3CO_2^-$

[0093] The table of an adduct ion mentioned above is used changing it by ionization mode (are they ESI or APCI?), the cation, or the anion. Since in what analysis mode the acquired data acquired this can understand if it is a data processor linking directly to the mass spectrometer, selection of a table can be performed automatically. Of course, you may choose the table memorized by the table 63 by external input meanses, such as a keyboard.

[0094] Moreover, two or more mass differences between a pseudo-molecular ion and two or more adduct-ion kinds are memorized on the kind of solvent used for mass analysis, the kind of ionization, and two or more storage tables divided for every polarity of a spectrum, and the analysis conditions of mass analysis can also constitute so that a suitable storage table may be chosen by the analysis section 62.

[0095] As mentioned above, also in the 2nd operation form of the explained this invention, the same effect as the 1st operation form can be acquired.

[0096] In addition, the situation of an adduct ion may also change according to a compound or analysis conditions. In this case, if a researcher analyzes the acquired data and a pseudo-molecular ion can be specified, this can be transmitted to the memory of a data processor and an addition table peculiar to a researcher can be made.

[0097] Moreover, although counted about the peak which did not consider the intensity of ion at all but only exceeded the threshold level about the calculus of the index of the degree of similar mentioned above, ionic strength can also be used as weight of this count.

[0098] Moreover, since many spectrums are already acquired, this can be integrated and this can also be made to memorize as a table in quest of an average pattern, although the case where the table of an adduct ion also disregarded ionic strength was explained. In this case, what is necessary is just to let the average of the ionic strength of two spectrum (table and acquired spectrum) ion to compare be weight.

[0099] What is necessary is to combine this result with a bar graph (bar graph), and just to display it on the displays 64, such as CRT, as a table, after the above molecular-ion presumption. Moreover, as shown in drawing 8 , a pseudo-molecular ion can be clearly shown by a pseudo-molecular ion and an adduct ion being shown with a bar thicker than other mass peaks so that a bar graph may understand the relation of a pseudo-molecular ion and an adduct ion.
[0100] Moreover, the rod of the same color may show the combination of a pseudo-molecular ion and its adduct ion, and another color may show the group of other pseudo-molecular ions. In short, a pseudo-molecular ion should just be clearly shown on a bar graph. Thereby, in the case of mixture, a situation can be more nearly intuitively grasped now.
[0101]
[Effect of the Invention] Since this invention is constituted as explained above, it has the following effects. Since it is constituted by the data processor so that a molecular ion may be presumed automatically, it can prevent a fault entering quickly and the mass analysis method and equipment which can presume the molecular weight of a pseudo-molecular ion, as a result a sample with high precision can be realized.
[0102] Furthermore, about an ion kind with the high frequency of occurrence, weighting is carried out automatically, and since it constitutes so that an adduct-ion table may be updated in an automatic hand, the mass analysis precision of the analysis object analyzed can be improved by each mass spectroscope. [many]
[0103] Moreover, presumption of a pseudo-molecular ion, as a result presumption of molecular weight can be performed regardless of the existence of experience of an analysis person. moreover . Since the combination of two or more compounds can be presumed also in mixture, waste of an analysis error and time can be prevented.

[Brief Description of the Drawings]
[Drawing 1] It is the outline block diagram of the mass spectroscope which realizes the mass analysis method which is the 1st operation gestalt of this invention.
[Drawing 2] It is the flow chart which shows operation by the whole analysis of the mass spectrum by the data processor of drawing 1 .
[Drawing 3] It is the graph which shows the mass spectrum acquired by atmospheric pressure ionization.
[Drawing 4] It is the graph which shows the mass spectrum to which threshold level processing and isotope processing were carried out.
[Drawing 5] It is the flow chart which shows detailed processing of search of a pseudo-molecular ion.
[Drawing 6] It is the operation flow chart of the mass analysis method which is the 2nd operation gestalt of this invention.

[Drawing 7] It is the graph which shows the mass spectrum of mixture.

[Drawing 8] It is the graph which showed the pseudo-molecular ion and the adduct ion by the bar graph thicker than other mass peaks.

[Drawing 9] It is the outline block diagram of the liquid chromatography direct connection mass spectrometer in the former.

[Drawing 10] It is the graph which shows an example of the mass spectrum acquired by atmospheric pressure ionization.

[Description of Notations]

1 Liquid Chromatograph (LC)

2 ESI Probe

3 Ion

4 Mass Spectrometer

6 Data Processor

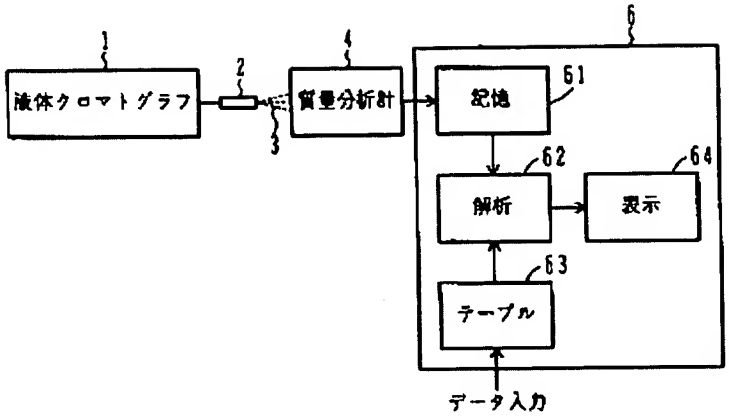
61 Storage Section

62 Analysis Section

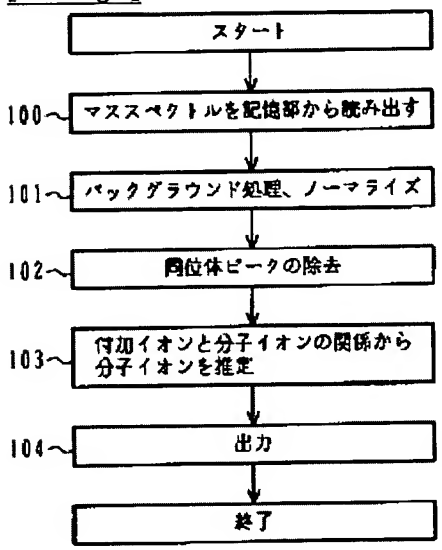
63 Table

64 Display

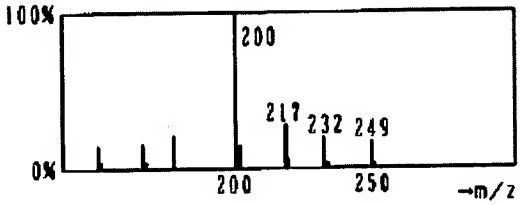
[Drawing 1]



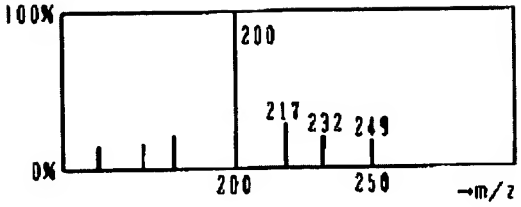
[Drawing 2]



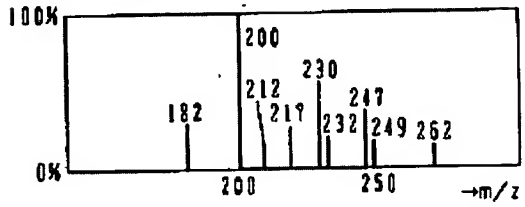
[Drawing 3]



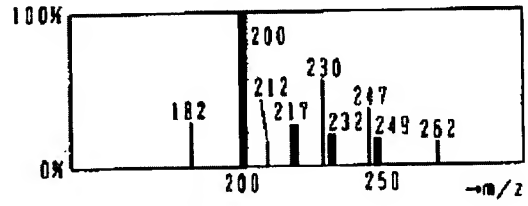
[Drawing 4]



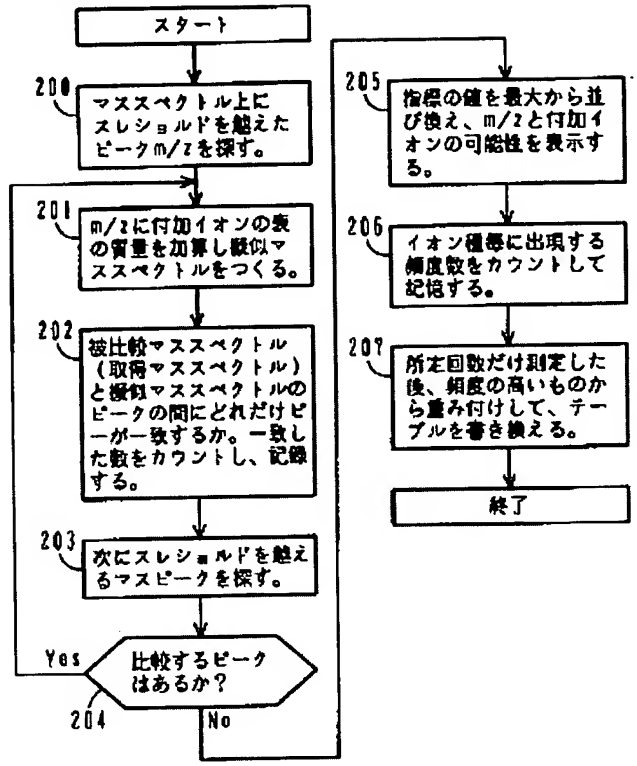
[Drawing 7]



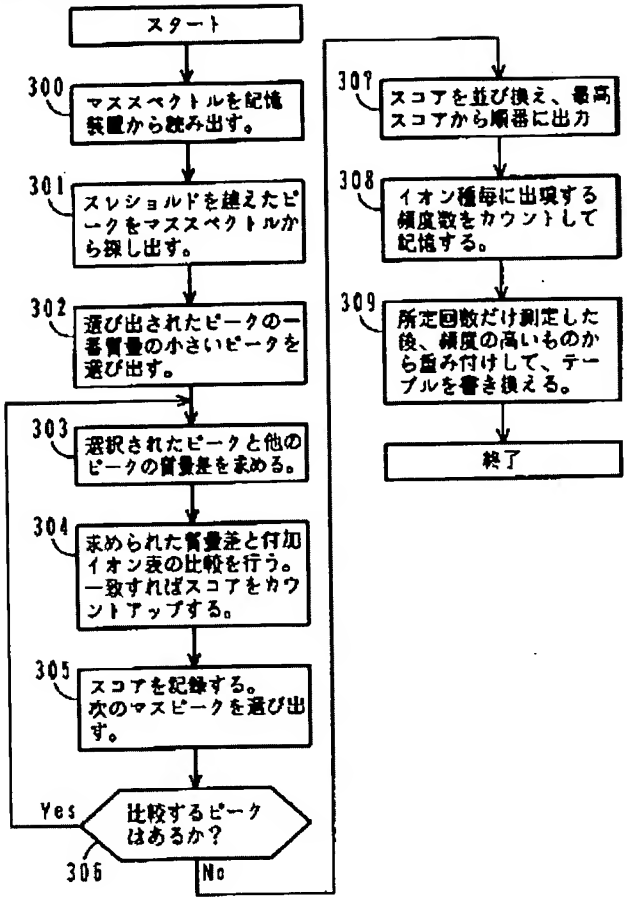
[Drawing 8]



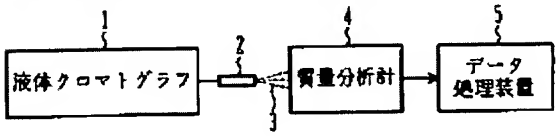
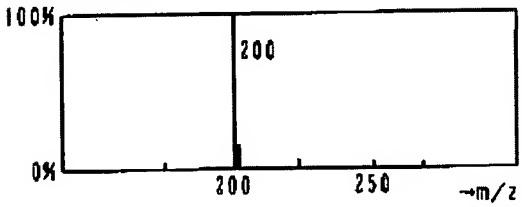
[Drawing 5]


スタート
200
マススペクトル上にスレショルドを越えたピークm/zを探す。
201
m/zに付加イオンの表の質量を加算し擬似マススペクトルをつくる。
202
被比較マススペクトル（取得マススペクトル）と擬似マススペクトルのピークの間にどれだけピークが一致するか。一致した数をカウントし、記憶する。
203
次にスレショルドを越えるマスピークを探す。
Yes
比較するピークはあるか？
204
No
205
指標の値を最大から並び換え、m/zと付加イオンの可能性を表示する。
206
イオン種毎に出現する頻度数をカウントして記憶する。
207
所定回数だけ測定した後、頻度の高いものから重み付けして、テーブルを書き換える。
終了

[Drawing 6]



[Drawing 9]



[Drawing 10]